BARD Final Report IS-4977-16R

Nanocomposite hydrogel membranes for fouling mitigation in wastewater reclamation for agricultural production

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Final Scientific Report

1. Overall summary and statistics

1.1. Abstract

Original objectives and changes: (i) Examine the physicochemical and mechanical properties of bulk and thin-film GO-polyampholyte nanocomposite hydrogels. (ii) Investigate the anti-adhesive (to organic macromolecules and bacteria) and antibacterial properties of thin-film composite (TFC)-GO hydrogels. (iii) Study the polymerization of TFC-GO hydrogels on UF membranes. (iv) Observe the organic and bacterial anti-adhesive properties, as well as the antimicrobial properties, of GO composite hydrogel membranes. (v) Evaluate the ability of GO composite hydrogel membranes to resist organic fouling and biofouling during filtration of secondary wastewater effluents and in a membrane bioreactor (MBR) system.

The research was performed in accordance with these objectives with the exception of one change: we studied the antifouling properties of one polyampholyte and not two as was originally proposed. Instead, we decided to focus on the antibacterial properties of the membranes functionalized with GO and GO nanocomposite. This change did not have any effect on the research directions nor on the research goals.

Background to the topic: Wastewater reuse is becoming an attractive option as a water resource for agricultural production. However, the effluent quality produced by conventional wastewater treatment technologies is still not high enough to be used for unrestricted irrigation. Membrane filtration is a promising technology for producing high-quality effluent. However, the vast application of membrane technology is hindered by membrane fouling. The goal of this project was to develop a dual antifouling and antibacterial ultrafiltration membrane with high resistance to organic matter adsorption and bacterial deposition for advanced wastewater treatment.

Major conclusions, solutions, achievements: We investigated and developed a thin-film zwitterion polyampholyte hydrogel grafted on UF membranes having excellent antifouling properties towards organic foulants. By incorporating antibacterial GO into the zwitterion hydrogel, the membrane also acquired antibiofouling properties. The antibacterial activity of GO was further enhanced by synthesizing ZnO nanoparticles (NPs) functionalized reduced GO (rGO–ZnO) nanocomposite. Incorporation of the rGO–ZnO nanocomposites into the membrane significantly inhibited biofilm formation compared to a pristine membrane. We also developed and investigated two methods enabling the attach GO to different UF membrane surfaces: (i) A novel photografting method to attach GO to the membrane surface following anchoring of benzophenone photoinitiator to GO surface; (ii). Bioinspired polydopamine chemistry to fabricate GO-functionalized membranes. Here, we studied two approaches - coating and blending - and elucidated the role of GO exposure on its bacterial toxicity. The last objective of the research, evaluating the long-term operation of selected membranes under real process conditions in an MBR system treating real domestic wastewater, is still ongoing.

Implications: The research provided new ways to develop antifouling UF membranes and to attach NPs to polymeric membranes surface. It also presented a new direction to enhance GO antibacterial activity as well as fundamental knowledge regarding the effect of the GO exposure on its bacterial toxicity. These findings can be used to develop ultra-low fouling polymeric membranes for wastewater treatment. The practical application of the new dual functionality membrane is currently being investigated. If successful, the energy consumption of these membranes for wastewater treatment and/or secondary effluent filtration, will be much lower than that of the current membranes. Thus, high quality reclaimed wastewater for agricultural usage can become feasible and economical.

Summary Sheet

Publication Summary

PubType	IS only	Joint	US only
Abstract - Presentation	0	1	0
Reviewed	1	4	0

Training Summary

Trainee Type	Last Name	First Name	Institution	Country

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1.3. Contribution of the collaboration

The research in most stages was conducted in close collaboration between the BGU and Yale groups and all the publications were written by both groups (except for the one published before the Yale group replaced the group from Johns Hopkins University). This was achieved through frequent skype meetings between both PIs and all the involved students, and by conducting complementary experiments in the collaborating laboratory. In addition, both PIs visited the collaborator’s laboratory during the second year of this project and met the students who worked on the project. Currently, the research and collaboration between the two groups are still ongoing, and the two PIs are also exploring ways to continue the collaboration in future research.

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1.2. Achievements

1.2.1. Membrane modification to reduce fouling and biofouling

As shown in Fig. 1, a polyampholyte (zwitterion) hydrogel was UV grafted to a PES membrane. The thickness of the grafting hydrogel layer was easily controlled by changing the UV irradiation time or intensity. Owing to the high hydration degree and neutral surface charge, the modified PES membrane (p-PES membrane) showed excellent antifouling properties for different foulants (e.g., protein, external polymeric substances and protein).

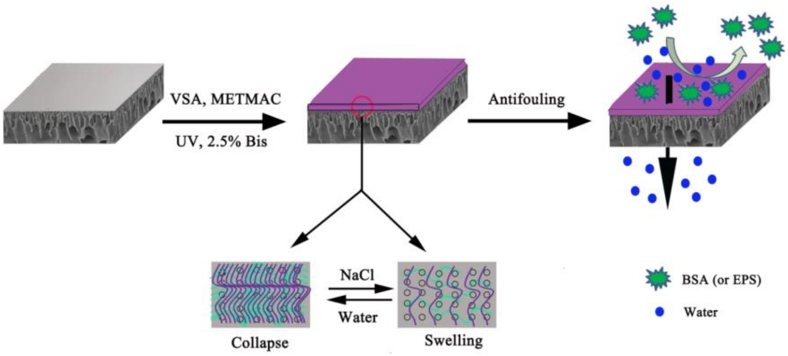

Fig. 1. The schematic illustration of PES membrane surface UV grafting with a new polyampholyte hydrogel layer. The optimized modification condition is: VSA: METMAC = 3:1 (molar ratios), cross-linker = 2.5% to total monomer concentration, UV time = 20 min. The modified membrane possesses the typical anti-polyelectrolyte behavior of zwitterion (i.e., a high flux in salt solution and low flux in water).

The attachment of the antibacterial GO nanosheets on the polysulfone membrane surface using polydopamine (PDA) chemistry was investigated (Fig. 2). It was found that the GO nanosheets were exposed on the surface of the GO-coating membrane is more antibiofouling compared to the GO-blending membrane. This was explained by the self-polymerization of dopamine on the surface of GO nanosheets that hindered the GO nanosheet exposure.

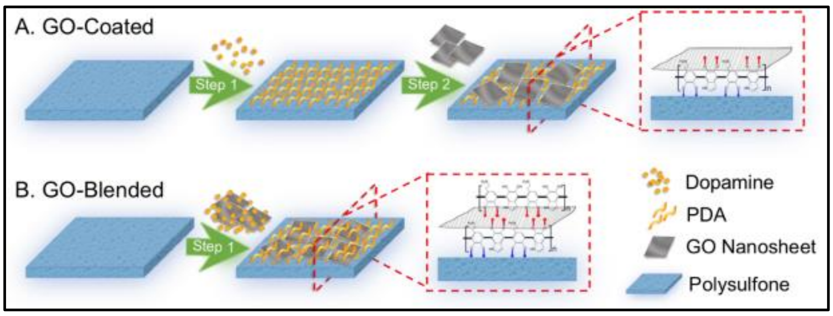

Fig. 2. Schematic illustrating the two modification strategies used to functionalize GO nanosheets on the surface of polysulfone membranes. (A) The procedure for the GO-coated strategy (more nanosheets are exposed on the surface). The dopamine monomer solution is poured on the membrane surface to form a nascent polydopamine (PDA) layer (Step 1), which could be further crosslinked under alkaline (basic) conditions to bind GO on the surface (Step 2). (B) The procedure for the GO-blended strategy (less expose). A mixture of dopamine and GO is in contact with the polysulfone surface to form a PDA/GO composite layer.

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We also developed a novel strategy for GO functionalization on PVDF and PSf membrane surface using benzophenone chemistry (Fig. 3). It was found that the GO nanosheets can be irreversibly grafted to any inert membrane surfaces via benzophenone-initiated cross-linking under ultraviolet irradiation. The GO-functionalized PVDF and PSf membranes exhibited strong antibacterial activity, reducing the number of *E. coli* viable cells by 90% and 75%, respectively, compared to the number with the pristine membranes.

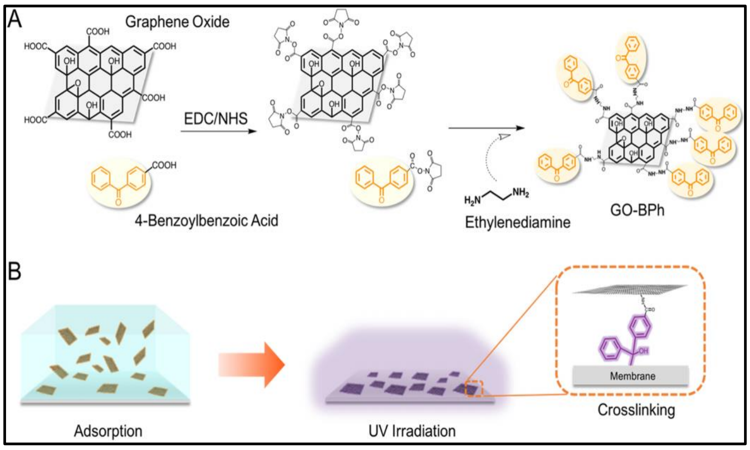

Fig. 3. Schematic diagram of the surface modification procedure using benzophenone chemistry. (A) Reaction procedure for synthesizing benzophenone-functionalized GO nanosheets. (B) Benzophenone functionalized GO nanosheets are first adsorbed on the membrane surface through hydrophobic interactions. Benzophenone groups are then covalently linked to the substrate membranes via photoinduced grafting and cross-linking under UV irradiation.

1.2.2. Development of dual functionality membranes

We introduced the antibacterial GO nanosheets to the low-fouling membrane (p-PES, Section 1.2.1) via vacuum filtration (see Fig. 4A). We demonstrated that a membrane with dual antifouling and antibiofouling activity was obtained. The dual functionality membrane displayed much less biofilm formation than the unmodified membrane. However, the antibacterial ability of GO is still unfavorable. Also, the loading amount of GO using vacuum filtration is low. In order to improve the antibacterial activity of GO, a one-step probe sonication method was used to functionalize GO with broad and high antibacterial ZnO NPs (rGO–ZnO nanocomposite). The contact killing results showed that rGO–ZnO nanocomposite possess much high antibacterial property compare to pure GO, and that the rGO–ZnO incorporated PES membrane presents an excellent antibiofouling property. Currently, we are investigating a new dual functionality membrane by UV grafting a thin zwitterion hydrogel layer on the rGO–ZnO incorporated PES membrane surface (Fig. 4B).

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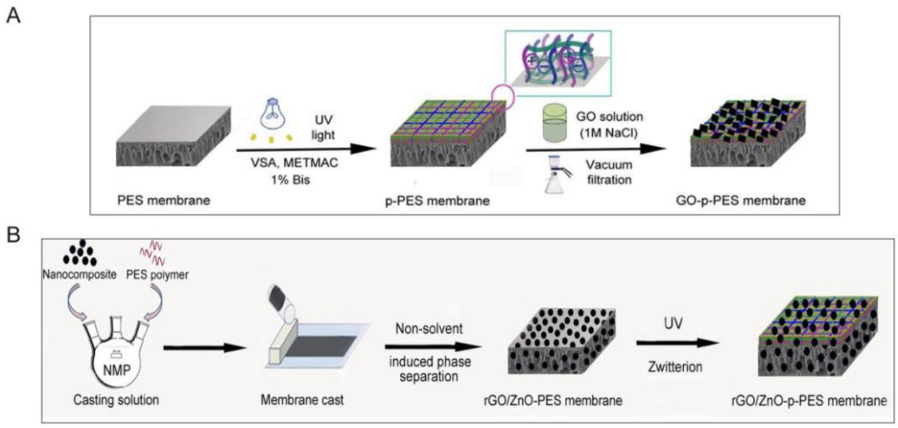

Fig. 4. Schematic diagram of two different methods used for membrane surface antifouling and antibacterial dual functionality modifications.

1.2.3. Long-term operation in MBR under real conditions

We are currently studying the long-term application of the dual functionality membrane in a lab-scale MBR system at BGU. The MBR (Fig. 5) is equipped with two membrane models and fed with real domestic wastewater from Sede Boker. Thus far (after 30 days), the modified membrane showed less transmembrane pressure (TMP) increase with filtration time, i.e., less fouling. This result indicates that the operation time without chemical cleaning can be increased by about 1.5 times compared to the pristine time. However, the modified membrane still fouled. Therefore, we are currently investigating the effect of the modification conditions on the antifouling properties of the membrane and investigating the antifouling mechanisms (e.g., biofilm structure and foulants composition) to further improve the membrane performance for a long-term operation and in real solutions.

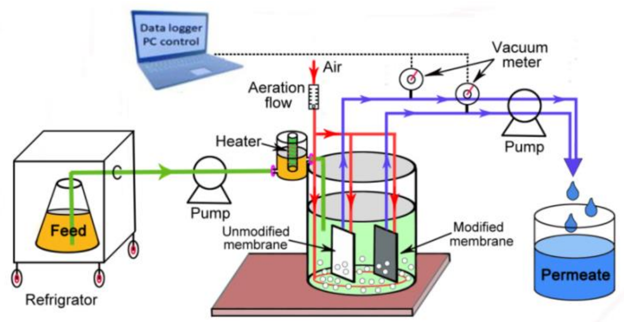

Fig. 5. The schematic diagram of the lab-scale MBR system. The filtration was performed under identical conditions and at a permeate flux of 60% of the critical flux. The transmembrane pressure (TMP) which directly reflects the membrane fouling was automatically monitored and recorded. HRT is 10 h, STR is 30 days and the MLSS concentration is 7000~9000 mg/L.

Publications for Project IS-4977-16R

Status	Type	Authors	Title	Journal	Vol:pg Year	Coun
Published	Reviewed				:	IS only
Published	Reviewed				:	Joint
Accepted	Reviewed	*Cheng, W.; Lu, X.; Kaneda, M.; Zhang W.; Bernstein, R.; Ma, J.; and Elimelech, M.*	Graphene Oxide Functionalized UF Membranes: The Importance of Nanosheet Surface Exposure for Biofouling Resistance	***Environmental science & technology***	: 2019	Joint
Accepted	Reviewed	*Kaneda, M.; Lu, X.; Cheng, W.; Zhou X.; Zhang W.; Bernstein, R.; Kimura, K.; and Elimelech, M.*	Photo-grafting Graphene Oxide to Inert Membrane Materials to Enhance Antibacterial Activity	***Environmental science & technology Letters***	6 : 141-147 2019	Joint
Published	Abstract - Presentation	*1. Zhang W., Cheng W., Lu X., Elimelech M., Bernstein R.*	Functionalization of ultrafiltration membrane with polyampholyte hydrogel and graphene oxide to achieve dual antifouling and antibacterial properties	***North American Membrane Society (2018), Kentucky, USA***	: 2018	Joint
Published	Reviewed	*Wei Zhang, Yang Yang, Eric Ziemann, Avraham Be'er, Muhammad Y Bashouti, Menachem Elimelech, Roy Bernstein*	One-step sonochemical synthesis of a reduced graphene oxide–ZnO nanocomposite with antibacterial and antibiofouling properties	***Environmental Science: Nano***	6 : 3080-3090 2019	Joint